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Feasibility and enhanced sequestration of CO_2 hydrate in ocean sediments

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ABSTRACT

As the problem of global warming becomes more serious, more efforts are needed to reduce CO_2 emissions, and CO_2 sequestration is considered to be one of the most effective ways to reduce greenhouse gases. The study of natural gas hydrates has become more innovative, with huge hydrate-forming zone (HFZ) that can be effectively used to sequester CO_2. In order to accurately characterize the formation and dissociation of CO_2 hydrate, we have fitted the hydrate phase equilibrium to precisely control the chemical reaction by temperature and pressure. By injecting CO_2 into the HFZ for 30 years, the permeability and porosity around the wellbore dropped to 1.55×10^{-3} mD and 0.056. Plugging occurred which prevented gas injection. Then we proposed thermal stimulation, increasing injection pressure and hydraulic fracturing to enhance sequestration. Thermal stimulation can restore stratigraphy conditions to initial conditions. The CO_2 was injected into the reservoir successfully with a sequestration volume of 5.50×10^7 m^3. Also, the injection rate decreased slowly, allowing for long-term sequestration. In contrast, the physical methods, such as increasing injection pressure and hydraulic fracturing, can only increase the rate for a short time, and the sequestration increased from 4.23×10^7 m^3 to 4.42×10^7 m^3 and 4.34×10^7 m^3, respectively. These results demonstrate that the most important measures to enhance sequestration by mitigating hydrate plugging are destabilizing hydrate and restoring injection loss.

Keywords: CO_2 hydrate; CO_2 sequestration; hydrate phase equilibrium; thermal stimulation

NONMENCLATURE

Abbreviations	
PR-EOS	Peng-Robinson equation of state
GMGS	Guangzhou Marine Geological Survey
HFZ	Hydrate-forming zone
Symbols	
g	Gas phase
l	Liquid phase
s	Solid phase
k	Effective permeability
φ	Porosity
K	Equilibrium values
k_1 to k_5	Correlation coefficients
P	Pressure
T	Temperature

1. INTRODUCTION

The oceans are the largest ecosystem on the planet and play an important role in mitigating climate change by absorbing large amounts of CO_2[1]. Carbon neutrality is now being considered by injecting CO_2 directly into the ocean[2]. The injection of CO_2 directly into the deep sea, due to its relatively high solubility and negative buoyancy, has led to the formation of lakes of CO_2 at the sea floor from liquid CO_2[3-5]. In addition, CO_2 hydrates are also easily formed under low temperature and high pressure conditions in the sea[6]. Among them, CO_2 hydrate is a cage-like crystal structure formed by CO_2 and water molecules, which can be used as a medium for long-term CO_2 storage[7].

The mechanism of CO_2 storage via hydrate has been studied by different methods. Teng et al.[8] analysed the feasibility of CO_2 sequestration under deep-sea

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conditions. They took different mechanisms into account, including the dynamics of dissolved components and their corresponding effects on hydrate formation and fluid flow. In intact deep-sea sediments, the hydrate cap formation in the hydrate-forming zone (HFZ) and the negative buoyancy effectively immobilise the injected CO_2. The main role of hydrate is to prevent upward flow of CO_2 due to buoyancy. Qureshi et al.[9] examined the effect of salinity on CO_2 hydrate stability in simulated deep-sea sediments to foster real-time field application. The experimental results indicated that CO_2 hydrates were adequately stable when submerged inside the brine solution. Qanbari wt al.[10] studied permanent trapping of CO_2 at a depth of a few hundred meters beneath the ocean floor. They reported numerical simulation studies that indicate that injection of CO_2 at a depth of approximately 800 m below the ocean floor leads to the rise of CO_2 until a depth of approximately 360 m below the ocean floor, where hydrates will form reducing the formation permeability. Zhang et al.[11] investigated the feasibility of storing CO_2 inside the hydrate stability zone by reservoir pressure management. Results showed that during CO_2 injection, CO_2 hydrate formation delayed CO_2 breakthrough and moderated reservoir pressure due to volume shrinkage thus allowing more CO_2 to be stored. Furthermore, over half of the CO_2 was stored as immobilized CO_2 hydrate which also limited post-injection migration of free CO_2 and leakage through the caprock. Gauteplass et al.[12] They et al. studied that the formation of solid hydrates in the near-wellbore region could lead to permeability damage and ultimately to injection loss. Thermal stimulation proved to be the most effective remediation method for near-zero permeability conditions.

In summary, the injection of CO_2 into the ocean has multiple mechanisms that work together. Among them, sequestration of CO_2 via hydrate is a long-term storage method. However, this may also lead to permeability damage and ultimately to injection loss. Therefore, it is necessary to investigate the feasibility of injecting CO_2 into the HFZ and enhancement of the sequestration. The paper is organized as follows. Firstly, we introduced the method of numerical simulation. Then, the analysis of the hydrate stability was mainly focused on. Secondly, we injected CO_2 into the HFZ, and plugging occurred around the wellbore. So we proposed various methods to enhance the sequestration, including thermal stimulation, increasing the injection pressure and hydraulic fracturing. Finally, the enhancement effects of these methods were analyzed.

2. NUMERICAL SIMULATION

2.1 Mathematical models

CMG is developed by the Canadian Computer Modelling Group ltd. for the numerical simulation of oil reservoirs. The simulator of CMG-STARS has calculation modules to deal with the change of phase state and chemical reaction kinetics. Many researchers have successfully applied the simulator to investigate hydrate reservoirs[13,14].

The generation of hydrate from CO_2 and water involves complex physical and chemical processes, including chemical reactions, multiphase flow and heat transfer. In order to establish the mathematical model, the following assumptions were considered: (1) The model contains only three phases (liquid, gas and solid) and three components (water, CO_2 and hydrate); (2) The flow of liquid and gas in porous media conforms to Darcy's law.

The process of hydrate formation and dissociation can be described as:

$$CO_2(g) + nH_2O(l) \leftrightarrow CO_2 \cdot nH_2O(s) \pm heat \quad (1)$$

The details and derivation of the mass balance equations, energy conservation equations and kinetic model of hydrate formation and dissociation for the model have been presented in our previous paper[15].

The relative permeability model and capillary pressure model refer to Li et al.[16]. With the formation of hydrate, the effective permeability of hydrate formation changes with the change of porosity. In this study, the relationship between effective permeability and porosity is based on the Carmen-Kozeny model[17]:

$$k = k_0 \left(\frac{\varphi}{\varphi_0}\right)^{\lambda} \left(\frac{1-\varphi_0}{1-\varphi}\right)^2 \quad (2)$$

Where k is the effective permeability when the porosity is φ; k_0 is the effective permeability when the porosity is φ_0; λ is an empirical parameter, λ=5.

In this study, the phase equilibrium is specified based on K values, which are derived from measured three-phase equilibrium data for pressure and temperature, calculated from thermodynamic models such as the Peng-Robinson equation of state (PR-EOS)[17]:

$$K = \left(\frac{k_1}{P} + k_2 \times P + k_3\right) \times exp\left(\frac{k_4}{T-k_5}\right) \quad (3)$$

Where k_1 to k_5 are correlation coefficients that vary with pressure P and temperature T. The variation of K controls hydrate formation and decomposition. Hydrate decomposition at K>1, hydrate formation at K<1.

2.2 Hydrate stability

The hydrate stability is the most important parameter for verifying hydrate formation and enhanced storage, an exact fit to this parameter is required.

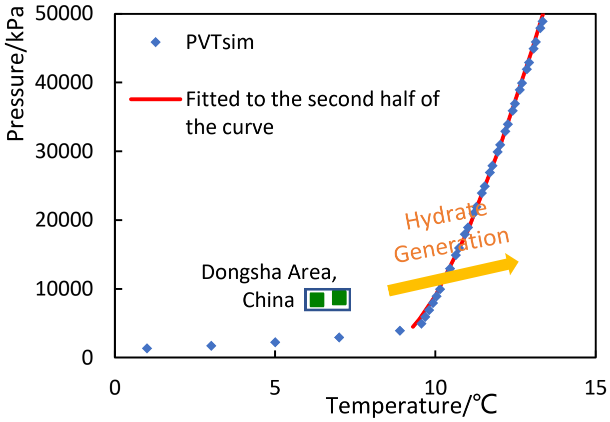

Fig. 1. Curves for fitting CO_2 hydrate phase equilibria

Fig. 1 shows the stability data of CO_2 hydrate obtained from our simulation by PVTsim software. We can regard the CO_2 hydrate stability curve as a combination of two curves: a low pressure curve and a high pressure curve. Fitting two curves with one equation is usually inaccurate. In 2013, the Guangzhou Marine Geological Survey(GMGS) conducted its second hydrate exploration program in the Dongsha Area[18]. The temperature and pressure in the GMGS2-8 allow for CO_2 storage via hydrate[19]. As CO_2 is injected to generate hydrate, heat is released by the chemical reaction. The temperature and pressure conditions will go through the high pressure curve. Therefore we believe that an accurate fit to the second half of the curve provides an accurate response to the stability of the hydrate.

To verify that the equation of state accurately controls whether hydrate is generated or not, a model of 100 m × 100 m × 100 m was built. The reservoir had an initial temperature of 10°C and an initial pressure of 8000 kPa, which did not reach the conditions for hydrate generation. We set up a water injection well in the centre of the model to control the pressure. In the first year no action was taken, in the second year water injection was started with an injection pressure of 12,000 kPa, in the third year injection was stopped and in the fourth year it became a production well to reduce the bottomhole pressure to 5,000 kPa. Fig. 2 shows the change in hydrate volume.

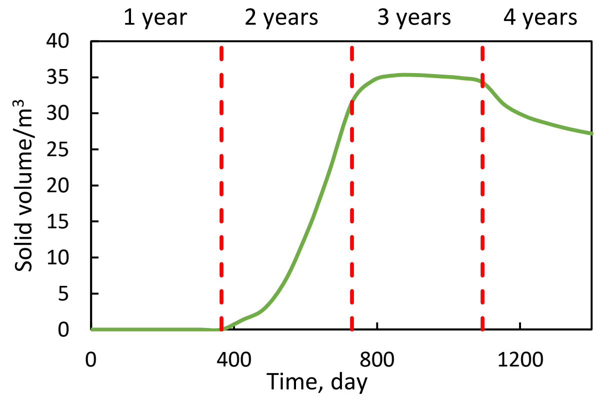

Fig. 2. Curve of hydrate volume change

Due to the fact that the initial temperature and pressure did not reach the conditions for hydrate stability, there was no hydrate generation in the first year without action. In the second year the injection pressure was raised and the pressure spread from the wellbore over an increasing area, resulting in the generation of hydrate at an increasing rate. Even in the third year, after injection had stopped, the high pressure allowed for continued hydrate generation. The hydrate did not dissociate until the pressure returned to initial pressure. In the fourth year we started to reduce the pressure, which was more conducive to the decomposition of the hydrate. With this conceptual model, an exact fit to the hydrate phase equilibrium can be validated.

2.3 Mathematical models

The numerical simulations we conducted for the study were based on the best available data from site GMGS2-8 in the Dongsha Area[19]. It is assumed that the hydrate content in HFZ is 0. We had developed a reservoir grid of 56 × 56 × 31, with a size of 560 m × 560 m × 105 m. The upper part is a 5m overburden and the lower part is a water layer. It is also assumed that the overburden and water layer are homogeneous. In the centre of the model there is an injection well. Fig. 3 shows the schematic diagram of the model. The other model input parameters are shown in Table 1.

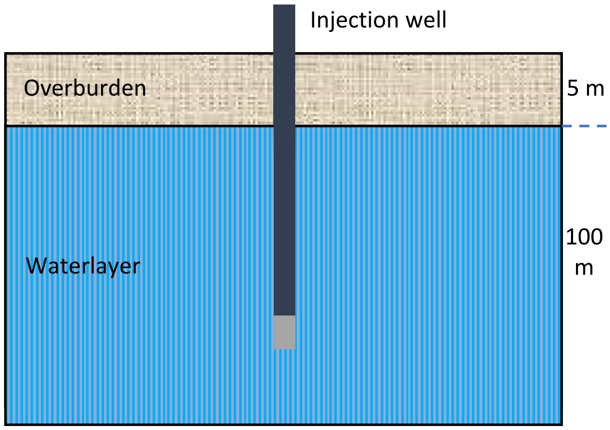

Fig. 3. Schematic diagram of the model

Table 1. Model Input Parameters for the Reservoir

Parameter	Value	Unit
Depth of sea	798	m
Depth of reservoir	58-163	m
Reservoir temp	6.61-8.95	℃
Reservoir pressure	8560-9080	kPa
Initial water saturation	1	
Compressibility	5.8e-7	1/kPa
Permeability	75	mD
Porosity	0.4	
Injection pressure	11000	kPa
Injection temperature	8.5	℃

3. RESULTS AND DISCUSSION

3.1 Hydrate Sequestration in HFZ

While the conversion of CO_2 to hydrates provides stable CO_2 sequestration, injecting CO_2 directly into the HFZ may also cause problems. We conducted a 30-year CO_2 injection into the reservoir and studied the effect on sequestration behaviour. Fig. 4 shows the distribution of the different parameters after 30 years of injection.

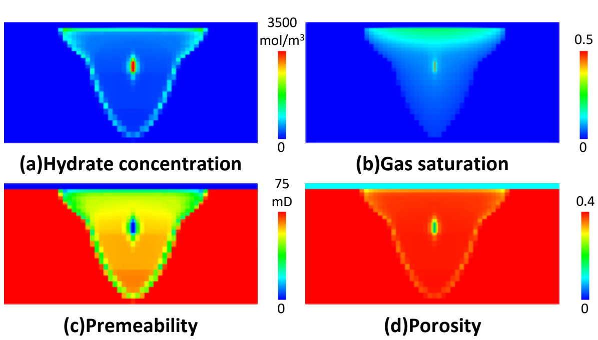

Fig. 4. Distribution of the different parameters after 30 years of injection

The CO_2 sequestration in the HFZ relied on the generation of hydrate at the CO_2 boundary to contain the gas and prevent leakage. The CO_2 then gradually changed to hydrate to achieve long-term sequestration. However, there was extremely high hydrate concentration and gas trapping around the wellbore. According to the simulation results, the porosity around the wellbore was 0.056 and the permeability was 1.55×10^{-3} mD when it came to the time limit, with heavily injection loss. This was similar to our other findings, where hydrate plugging occurred preventing CO_2 sequestration in the HFZ.

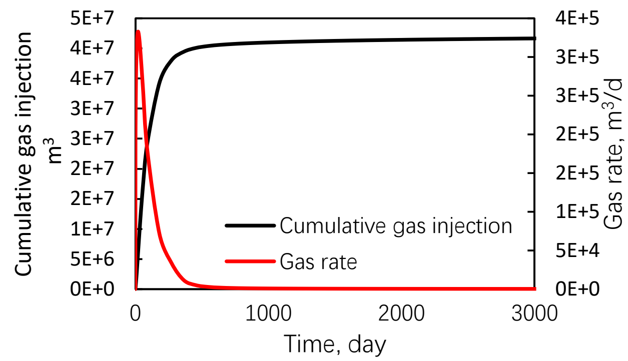

Fig. 5. Curves of cumulative gas injection and gas rate

Fig. 5 shows the variation in the amount of sequestration. The cumulative sequestration over 30 years of injection is 4.23×10^7 m^3. Within two years of injection, the injection rate had dropped to a very low level. We proposed a series of methods to eliminate the effects of plugging and began to implement them in the third year.

3.2 Thermal stimulation

Because of hydrate plugging, we performed thermal stimulation in the third year, raising the injection temperature to 12°C. Fig. 6 shows the change in cumulative gas injection and injection rate after thermal stimulation. And Fig. 7 shows the distribution of hydrate concentration.

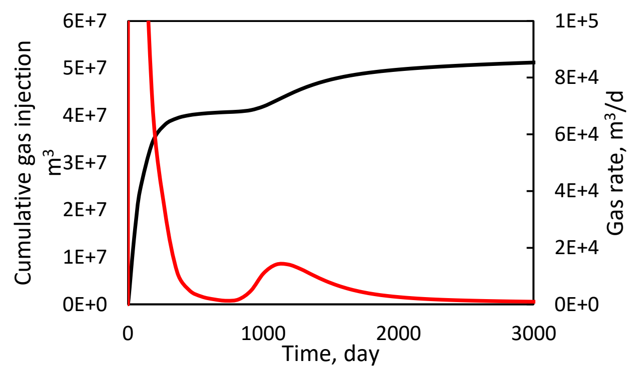

Fig. 6. Curves of gas injection by thermal stimulation

As shown in Fig.6, when the injection pressure was constant, the gas injection rate increased significantly after the third year of thermal stimulation. The gas injection rate increased from 1319 m^3/d to 14102 m^3/d. Also, the subsequent injection rate decreased more slowly, facilitating long-term injection. According to the variation of hydrate concentrations in Fig. 7, the hydrate was dissociated around the wellbore by thermal stimulation, mitigating the injection loss due to plugging. Figure 8 similarly showed the restoration of injection capacity by thermal stimulation. Analysis of permeability and porosity showed that flow capacity around the wellbore had been fully restored to initial reservoir conditions. Therefore thermal stimulation is an effective way to enhance CO_2 sequestration without injection loss.

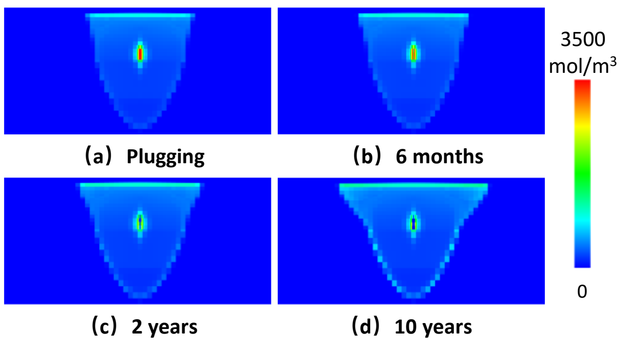

Fig. 7. Distribution of hydrate concentration after thermal stimulation

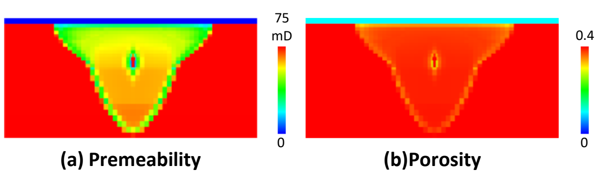

Fig. 8. Distribution of permeability and porosity after injection for 30 years

3.3 Increasing injection pressure

In general, to inject CO_2 into the reservoir, increasing the injection pressure is the most effective way in order to enhance the sequestration. We increased the injection pressure to 13000 kPa from the third year of injection. Fig. 9 shows the variation of sequestration with or without increasing the pressure.

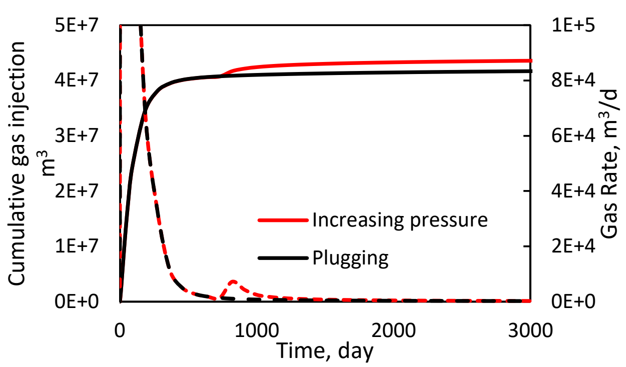

Fig. 9. Comparison curves with increased injection pressure (----represents the gas rate; ——represents the cumulative gas injection)

From Fig. 9, it can be seen that after increasing the injection pressure, the cumulative gas injection increased by a certain degree, from 4.23×10^7 m^3 to 4.42×10^7 m^3. However, by observing the variation of the gas injection rate, there was a significant enhancement only when the pressure was just increased. Then the rate quickly decreased and the duration of continuous injection was even shorter than at the beginning of the injection. Since hydrate plugging had already existed around the wellbore, the increase in injection capacity without disrupting hydrate stability was limited. In addition, increasing the injection pressure was also more conducive to hydrate generation, so the injection rate would drop more quickly. Although increasing the injection pressure is a favorable option for geological sequestration, sequestering CO_2 in the HFZ still requires other methods.

3.4 *Hydraulic fracturing*

In the process of gas hydrate production, hydraulic fracturing has also been widely studied. Before the sequestration process started, we set up a 0.1 × 110 m fracture at the injection well with the transmissibility multipliers of 10.

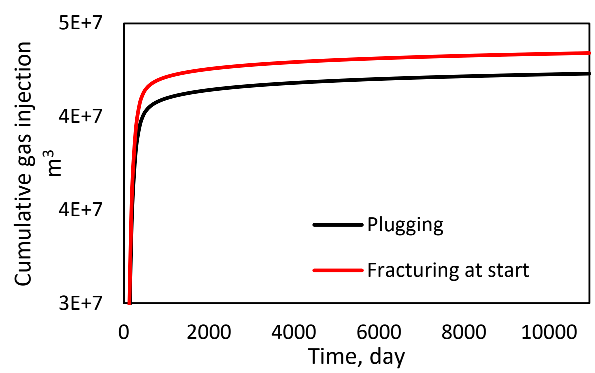

Fig. 10. Curves of sequestration at different times of fracturing

Fig. 10 shows the amount of sequestration performed at different times of fracturing. If we performed hydraulic fracturing before injecting CO_2, there would be a significant improvement in sequestration, up to 4.34×10^7 m^3. Then, as in the case without fracturing, the injection rate decreased rapidly. The continuous injection was minimal, with 96.5% of the total injection in the first two years. Therefore, this method is not sustainable and is not a viable method for long-term sequestration.

4. CONCLUSIONS

In this work, we analyzed methods to enhance the sequestration of CO_2 in the HFZ. First of all, hydrate phase equilibrium is an important factor to ensure CO_2

sequestration via hydrate, so we fitted the phase equilibrium curve accurately and verified it. Then, by injecting CO_2 into the HFZ, the permeability and porosity were reduced to 1.55 × 10^{-3} mD and 0.056, respectively.Plugging occurred around the wellbore. Thermal stimulation is effective in mitigating hydrate plugging. Increasing the injection temperature could return the stratigraphic conditions to the initial, ensuring the feasibility of long-term CO_2 sequestration. In contrast, both increasing injection pressure and hydraulic fracturing could only temporarily increase the injection rate. The above results indicate that the physically based methods are of limited contribution to enhance the sequestration, and the enhancement methods that inhibit hydrate stability are more advantageous for sequestration.

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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